

**FABRICATION OF SMART GLASS ELECTROCHROMIC DEVICE
USING RF MAGNETRON SPUTTERING**

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A project report submitted in partial
fulfillment of the requirement for the award of the Degree of Master of Electrical
Engineering



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JANUARY 2014

Special dedication with full gratitude on the guidance and encouragement from my beloved family and not to forget my supervisor who contributed opinions and ideas.



ACKNOWLEDGEMENT

Alhamdulillah, thank you Allah for giving me chance to finish my thesis. Foremost, I would like to express my sincere gratitude to my supervisor Dr. Mohd Zainizan Sahdan and my co-supervisor Assoc. Prof. Dr. Nafarizal Nayan for the continuous support for my master study and research, for their patience, motivation, enthusiasm, and immense knowledge. Their guidance helped me in all time during my research and writing this thesis.

Besides my supervisor, I would like to thank my fellow labmates and technicians in Microelectronics & Nanotechnology Shamsuddin Research Centre, UTHM for the stimulating discussions, tutoring and helps.

Not forgetting to my husband; Muhammad Fakhruddin Ismail, my daughter; Nur Hana Alisha and all family members who always support and give me courage to finish this study, without them it is impossible for me to stand where I am now.

ABSTRACT

Electrochromic device is an important functional device to control the amount of light through a glass. It usually used in sunlight control window glazing for buildings and automobile. The important feature of electrochromic glass is the ability to response toward the apply voltage in shortest time, and endurance to maintain in color shape after apply voltage. In this thesis, the oxygen gas percentage is optimized during the fabrication of tungsten trioxide (WO_3) as an electrochromic glass for window glazing application by using RF magnetron sputtering. The oxygen flow rate for the deposition is varied from 10sccm -22sccm which is 25%, 27%, 30%, and 35% of oxygen flow. The structures of WO_3 were investigated using X-Ray diffraction, Field effect scanning electron microscopy (Fe-Sem) and Atomic force microscopy (AFM). The electrochromic properties were characterized by a cyclic voltammogram and UV-Vis absorption spectra. The results show that nanocrystalline film with particle size of 51.54nm was deposited at 27% oxygen flow rate has the largest charge capacity and coloration efficiency among the others. The time respond taken for complete coloration at 4V is 2second. This result is a starting point for future work such as optimizing the film thickness or doping by other metals.

ABSTRAK

Filem nipis elektrokromik adalah alat yang sangat penting untuk mengawal jumlah cahaya yang melalui cermin kaca. Ia biasanya digunakan pada bangunan dan kenderaan untuk mengawal kemasukan cahaya didalam bangunan atau kenderaan. Ciri-ciri yang penting dalam elektrokromik adalah keupayaan untuk bertindak balas pada aliran voltan dalam masa yang singkat, dan ketahanan untuk mengekalkan bentuk warna selepas dikenakan sejumlah voltan pada sampel. Dalam tesis ini, gas oksigen telah di optimum dalam menghasilkan tungsten trioksida (WO_3) sebagai filem nipis elektrokromik untuk aplikasi tingkap kaca dengan menggunakan RF magnetron sputtering. Kadar aliran oksigen untuk pemendapan WO_3 adalah 10sccm-22sccm iaitu 25%, 27%, 30%, dan 35% aliran oksigen. Struktur WO_3 disiasat menggunakan X-Ray diffraction, Field effect scanning electron microscopy (Fe-Sem) dan Atomic force microscopy (AFM). Sifat elektrokromik telah dikenal pasti oleh cyclic voltammogram dan UV-Vis absorption spectra. Kajian ini mendapati filem nanocrystalline dengan saiz zarah 51.54nm didepositkan pada 27% kadar aliran oksigen, mempunyai kapasiti caj lebih besar dan kecekapan warna yang tinggi berbanding dengan filem-filem yang lain. Masa untuk filem bertindak balas kepada warna diambil pada 4V adalah 2saat. Keputusan ini adalah satu titik permulaan untuk kerja-kerja masa depan seperti mengoptimumkan ketebalan filem atau doping dengan logam lain.

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LIST OF SYMBOLS AND ABBREVIATIONS

EC	-	Electrochromic
WO ₃	-	Tungsten trioxide
NiO	-	nickel oxide
MoO ₃	-	molybdenum trioxide
IrO ₃	-	iridium trioxide
W	-	Tungsten
Ti	-	Titanium
V	-	Vanadium
Nb	-	Niobium
Ta	-	Tantalum
Mo	-	Molybdenum
Cr	-	Chromium
Mn	-	Manganese
Fe	-	Iron
Co	-	Cobalt
Ni	-	Nikel
Rh	-	Rhodium
Ir	-	Iridium
CVD	-	chemical vapor deposition
LiClO ₄	-	Lithium perchlorate
PC	-	Propylene carbonate
NiOOH	-	Nickel oxyhydroxide
HCl	-	Hydrochloric acid
NaOH	-	Sodium hydroxide

IZO	-	Aluminum doped zinc oxide
FTO	-	fluorine-doped tin oxide
FE-SEM	-	Field emission scanning electron microscope
AFM	-	Atomic force microscope
XRD	-	X-Ray diffraction
UV-Vis	-	UV-Visible Spectroscopy



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PTTA UTHM
PERPUSTAKAAN TUNKU TUN AMINAH

CHAPTER 1

INTRODUCTION

1.1 Introduction to electrochromic material

Electrochromic (EC) glass is a device that can change color when apply some voltage to the film. EC device consist of two EC layers separated by an electrolytic layer, conducting electrodes are used on both EC layers. Figure 1.1 show the basic structure of EC device embodies six superimposed layers on two substrates. First substrate consists of four layers as working electrode and the other substrate consist of two layers acting as counter electrode. Both substrates are then separated by electrolyte in a laminated configuration.

Working electrode usually made from mixed conductor, it acting as ion-storage layer and conduct ions and electrons. Optical absorption occurs when electrons move into the EC layers from the transparent conductors along with charge balancing ions entering from the electrolyte.

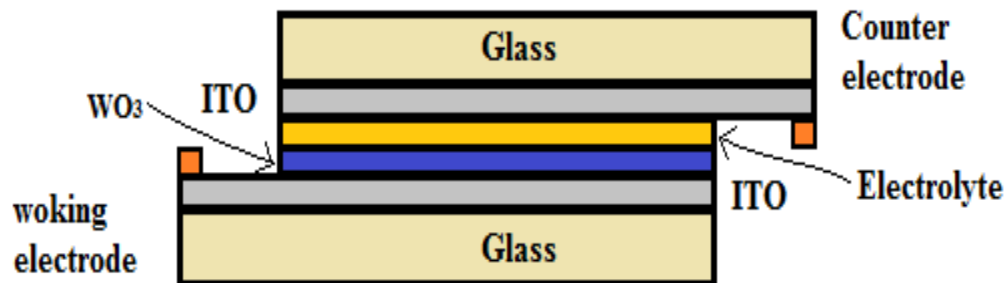


Figure 1.1: Electrochromic device configuration consist of two substrates divided by electrolyte.

Electrochromic (EC) becomes a whole wide attention among scientists since 40 years ago. However, electrochromism has remained an active area for basic and applied research, with large possibilities for applications in emerging technologies. The interest was boosted in the mid-1970s with the realization that electrochromisms was of much interest in fenestration technology as a means to achieve energy efficiency in buildings [1]. The application of electrochromic smart glass include transmittance modulation of sunlight control window glazing for buildings, optical display, and reflectance modulating automobile rear view mirrors [2].



Figure 1.2: Electrochromic Smart window used in a bulding [3]

Electrochromic (EC) materials are able to change their optical properties by changing the electrical voltage supply. Transition metal such as tungsten trioxide (WO_3), nickel oxide (NiO), molybdenum trioxide (MoO_3), and iridium trioxide (IrO_3) have been widely studied for used in electrochromic materials [4]. The electrochromic (EC) material will change their optical properties when charge insertion and this may cause the material change color or its opacity. Materials that change color upon insertion are called cathodic while a material that change color upon extraction called anodic. Metal oxide of W, Ti, V, Nb, Ta and Mo exhibit cathodic electrochromism and oxides of V,

Cr, Mn, Fe, Co, Ni, Rh and Ir are anodic electrochromism [5]. An amount of voltage needed to change its opacity, however once the glass change color, no electricity is needed for maintaining the particular shade which has been reach.

Method for preparing this electrochromic films include sputtering, spray pyrolysis, chemical vapor deposition (CVD), electrodeposition and sol-gel deposition. Figure 1.3 show the general schematic for spray pyrolysis, spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituent react to form a chemical compound. The chemical compound is volatile at the temperature of deposition. The process is a particularly useful for the deposition of oxides and has long been a production method for applying a transparent electrical conductor [6].

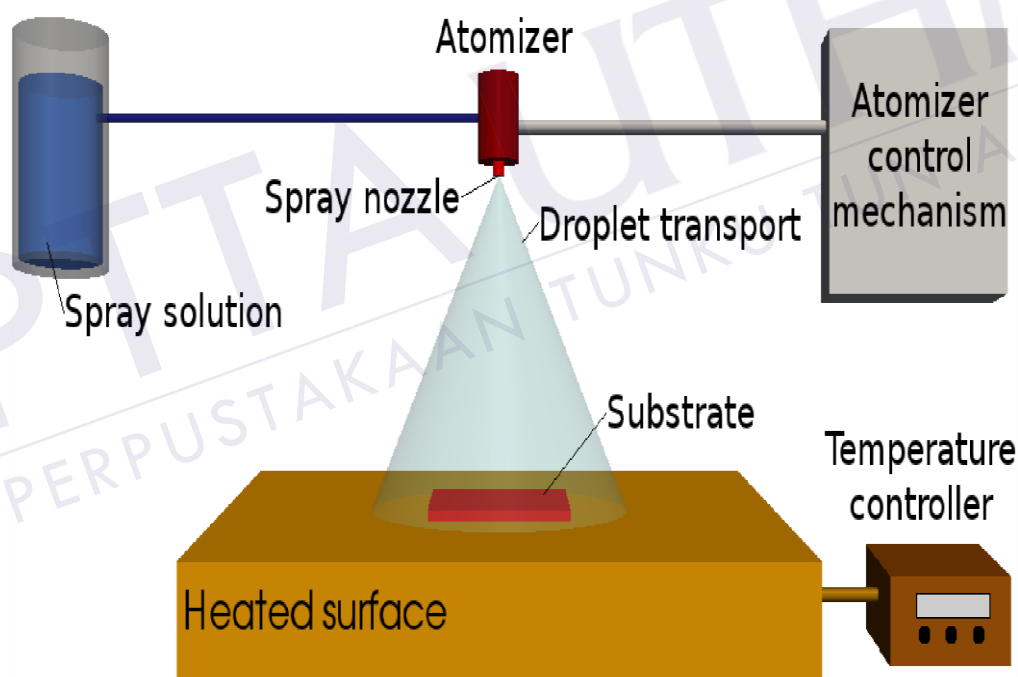


Figure 1.3: General schematic of a spray pyrolysis deposition process [7]

Chemical vapor deposition (CVD) is a chemical process used to produce high quality, high-performance, solid materials. The majority of its applications involve applying solid thin-film coatings to surfaces, it has been used to deposit a very wide range of materials. CVD also has a number of disadvantages. One of the primary disadvantages lies in the properties of the precursors. Ideally, the precursors need to be volatile at near-room temperatures [8]. Figure 1.4 illustrated the general process of CVD.

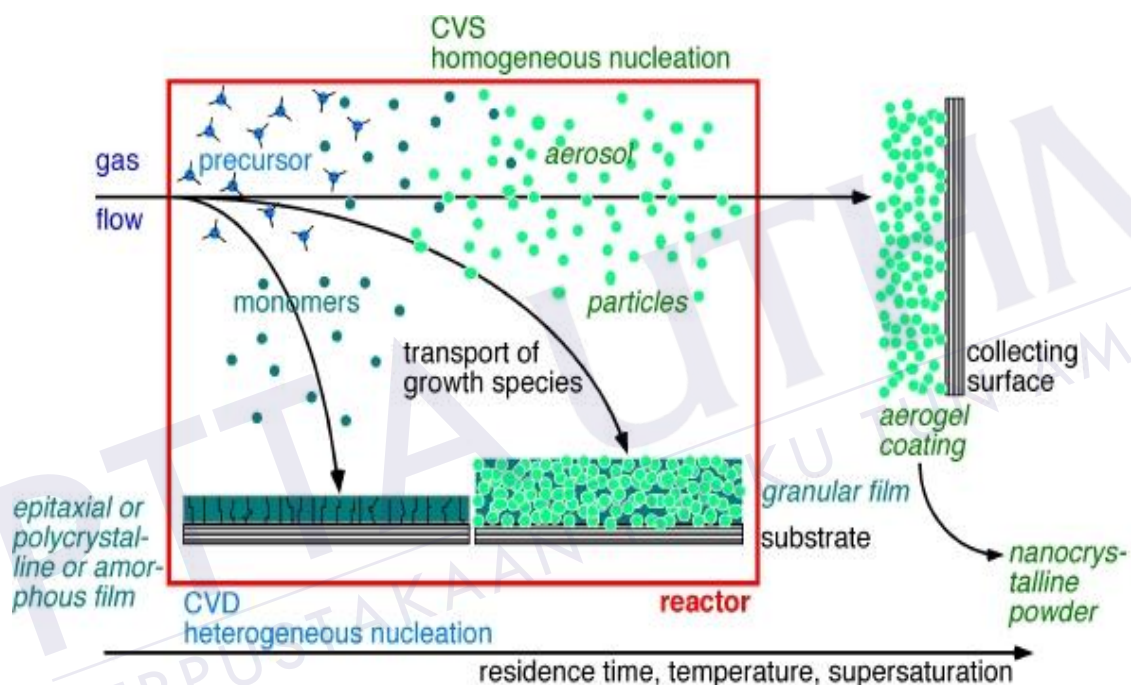


Figure 1.4: General schematic of chemical vapor deposition process [9].

Among those methods, reactive magnetron sputtering widely used to obtain WO_3 with good electric flow and optical properties. Sputtering is the process when an atom with enough energy bombarded into particles and produces an ion. The momentum transfer from the particles to the surface atoms can impart enough energy to allow the outer electron to escape from its orbit. Once ejected, these ion can travel to a substrate and deposit as a film. So in sputtering, the target material and the substrate is placed in a vacuum chamber. A voltage is applied between them so that the target is the cathode and the substrate is attached to the anode.

Plasma is created by ionizing a sputtering gas, generally a chemically inert, heavy gas like Argon. Figure 1.2 illustrate ionization process that creates plasma, the sputtering gas which is Argon ion will bombards the target and the target ion will deposit into substrate. Ions can be generated by the collision of neutral atoms with high energy electrons. The interaction of the ions and the target are determined by the velocity and energy of the ions, since ions are charged particles, electric and magnetic fields can control these parameters. The process begins with a stray electron near the cathode is accelerated towards the anode and collides with a neutral gas atom converting it to a positively charged ion. The process results in two electrons which can then collide with other gas atoms and ionize them creating a cascading process until the gas breaks down.



Figure 1.5: plasma ionization created during fabrication of Magnetron sputtering process [10].

The breakdown voltage depends on the pressure in the chamber and the distance between the anode and the cathode. At too low pressures, there aren't enough collisions between atoms and electrons to sustain plasma. At too high pressures, there so many collisions that electrons do not have enough time to gather energy between collisions to be able to ionize the atoms.

1.2 Problem statement

An attempt to fabricate a high efficiency electrochromic glass using tungsten oxide WO_3 is increasing extensively due to high color efficiency study by researchers. However, the electrochromic films cannot change color simultaneously in time even though the film is supposed to change, most of the eletrochromic devices are completely change color after 15 minutes [24]

1.3 Motivation

By changing the oxygen percentage would create defect in the WO_3 structure, and changing the performance of electrochromic device.

1.4 Objectives

Objective for this research is to fabricate electrochromic thin film using tungsten target using RF magnetron sputtering method and $\text{LiClO}_4 + \text{PC}$ as electrolyte. Oxygen flow of RF magnetron sputtering chamber was change to improve the performance of the device.

This research embarks on the following objectives:

- a) To fabricate a fast color response of electrochromic WO_3 thin films
- b) To get a low transmittance for blench state and color state of films after test voltage.

1.5 Scope of project

The main scope of this project is to investigate characterization of tungsten trioxide as electrochromic material. The scopes include:

1. To fabricate WO_3 film using pure 99.99% tungsten target using RF magnetron sputtering
2. To change parameter of oxygen flow to get high efficiency based on time respond of electrochromic WO_3 thin film.
3. To investigate the properties of WO_3 thin film deposited at various oxygen flow by using FE-SEM, AFM, XRD and two point probe.

1.6 Thesis Organization

This thesis consist of five chapter, the first chapter of this thesis consist of introduction to electrochromic material, this part explained about general overview of electrochromic smart glass based on first discovery, application and suitable material to produce this smart glass. Next section is about background study, problem statement, objectives, motivation, and scope of project and thesis organization. Second chapter is literature review consist of History, principle operation of electrochromic trioxide (WO_3) development, WO_3 thin films properties, and RF magnetron sputtering system. For third chapter, it consist of methodology on fabricating the WO_3 thin film using RF magnetron sputtering and introduce to the apparatus used to measure the characteristic of WO_3 materials. Chapter four consist of discussed about result and discussion of experiment and the last chapter is about conclusion to this research and future recommendation for future good. This thesis ended by references used during this research and Appendix for this thesis.

CHAPTER 2

LITERATURE REVIEW

This chapter consists of historical method and technology development for preparing electrochromic thin films, fabrication method, tools, and characterization equipment. This chapter may help to understand this project through basic theory.

2.1 History

Smart glass or switchable glass also called smart windows or switchable windows, it is refer to glass that changes light transmission properties under the application of voltage, heat or light. The glass blocking certain or all wavelength of light to pass through and it change into two conditions which are colored or bleached. Smart glass technologies include electrochromic, photochromic, thermochromic, suspended particle, micro-blind and liquid crystal devices [11] become interested among researcher.

The basic concept behind all smart windows is the same, they can be made in several different ways, each with a different method and properties for blocking light. Critical aspects of smart glass include material costs, installation costs, electricity costs and durability, as well as functional features such as the speed of control, fastest response, possibilities for dimming, and the degree of transparency.

An electrochromic window has a double-sandwich of thin layers, a separator in the middle, two electrodes act as electrical contacts on either side of the separator, and then two transparent electrical contact layers on either side of the electrodes. The basic working principle involves lithium ions acting as positively charged lithium atoms with

missing electrons that migrate back and forth between the two electrodes through the separator.

Normally, when the glass is clear, the lithium ions reside in the innermost electrode. When a small voltage is applied to the electrodes, the ions migrate through the separator to the outermost electrode where they scatter away most of the incoming light and turn the glass opaque. They remain there by themselves until the voltage is reversed, causing them to move back so the glass turns transparent once again. This process can be illustrated by figure 2.1 below. The power only needed to change them from one state to the other and no power is needed to maintain the windows in color or opaque state. The general EC phenomena of WO_3 due to the formation of tungsten bronze (M_xWO_3) according to the equation below where M^+ is H^+ , K^+ , Li^+ , or Na^+ .

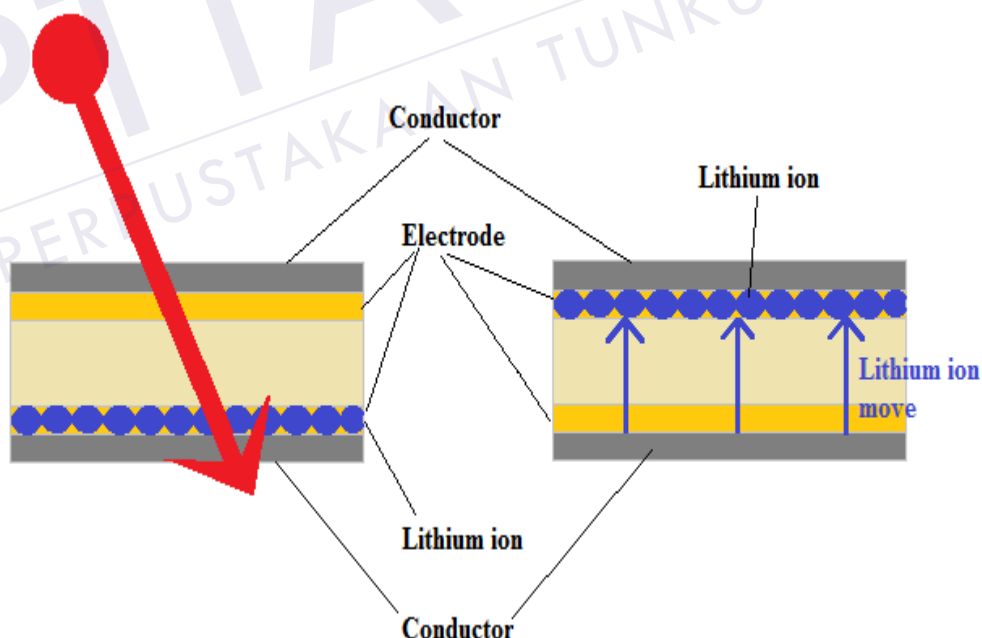
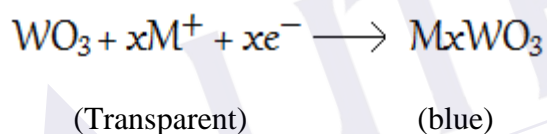


Figure 2.1: How electrochromic glass work

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